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 $\alpha,\alpha,\gamma,\gamma$ -Bisdiphenylene- β -phenyl Allyl and its Derivatives
(Commemoration Issue Dedicated to Professor Eiji Suito on
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ESR and ENDOR Spectra of Organic Stable Free Radicals: $\alpha, \alpha, \gamma, \gamma$ -Bisdiphenylene- β -phenyl Allyl and its Derivatives

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Electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) spectra of $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -phenyl allyl radical and of its derivatives have been observed and their hyperfine splitting constants and spin density distributions have been determined. The hyperfine splittings of the protons of the aryl group attached to the β -carbon of the allyl skeleton have been first observed. At low temperatures below -85°C their allyl skeletons in toluene solutions twist unsymmetrically on either side and the activation energy of the torsional vibration of the allyl skeleton is estimated to be about 2.5 Kcal/mol.

INTRODUCTION

The history of an organic stable free radical dated from 1900 when Gomberg¹⁾ published his discovery of the first organic stable free radical, triphenyl methyl. Thereafter, in 1923 Ziegler²⁾ presented several tetraaryl allyl radicals. One of the tetraaryl allyl radicals, $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -phenyl allyl (BDPA), was presented by Koelsch³⁾ in 1932. Recently, Kuhn *et al.*⁴⁾ have reported the synthesis of several BDPA-type radicals. These BDPA-type radicals are very stable. Many studies about these radicals in the solid state, such as magnetic susceptibility⁵⁾ or specific heat measurements,⁶⁾ have been published. However, there have been only a few reports about their electron spin resonance (ESR) spectra which consist of very broad lines in comparison with the spectra of $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene allyl (BDA) and $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -azo allyl (BDAA). Therefore, it is not clear whether an unpaired electron spreads all over the molecular frame, especially to the aryl group attached to the β -carbon of the allyl skeleton (β -aryl group). Kuhn *et al.*⁴⁾ supposed that the broadened line shapes of their ESR spectra are due to the small hyperfine splittings of the β -aryl protons. Maruyama *et al.*⁷⁾ assumed the spin delocalization to the β -aryl group in order to interpret the number of small hyperfine splittings in the ESR spectrum of $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -p-tolyl allyl (p-Me-BDPA). However, the hyperfine splitting constants of the β -aryl protons have never been obtained. Most recently, the authors⁸⁾ and McDowell *et al.*⁹⁾ have confirmed the existence of the small hyperfine splittings.

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ings due to the β -aryl protons from electron nuclear double resonance (ENDOR) measurements. Further, the authors observed the temperature dependence in the ENDOR spectra of BDPA-type radicals and their temperature-dependent ENDOR spectra were explained by torsional vibration of the twisted allyl skeleton.

In this paper, we shall report the results of the ESR and the ENDOR measurements of the BDPA-type radicals, and discuss about the proton hyperfine splitting constants and the dynamic behavior of the allyl skeleton in some detail.

EXPERIMENTAL

BDPA, *p*-Me-BDPA, $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -anisyl allyl (*p*-MeO-BDPA), $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -*p*-chlorophenyl allyl (*p*-Cl-BDPA), $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -*p*-bromophenyl allyl (*p*-Br-BDPA), $\alpha, \alpha, \gamma, \gamma$ -bisdiphenylene- β -*p*-biphenyl allyl (*p*-Phe-BDPA), BDA, BDAA, and $\alpha, \alpha, \gamma, \gamma$ -tetraphenyl allyl (TPA) (Fig. 1) were prepared following the process described in Refs. 2, 4, 10, and 11. Their physical constants and the results of the elemental analyses are shown in Table I. Toluene and liquid paraffin used as solvents were well purified, dehydrated, and degassed. The ESR spectra were measured with JEOL Model EM-3 and PE-3 X-band ESR spectrometers in the temperature range from -100 to $+100^\circ\text{C}$ for the toluene solutions and from 55 to 210°C for the liquid paraffin solutions. An aqueous solution of peroxyamine disulfonate was used as a standard of the magnetic field.¹²⁾ The ENDOR spectra were measured by a JEOL ES-EDX I spectrometer operating with 80 Hz magnetic field modulation in the temperature range from -110 to -40°C for the toluene solutions and from 55 to 80°C for the liquid paraffin solutions. The 150 watts CW RF field (6.5 KHz frequency modulation) was introduced to the coil inside the cavity for nuclear magnetic resonance (NMR) excitation. Each hyperfine splitting constant was determined by averaging the values obtained from two or three times of measurements. The simulation of the spectra and the molecular orbital (MO) calculations were carried out at the Kyoto University Computer Center.

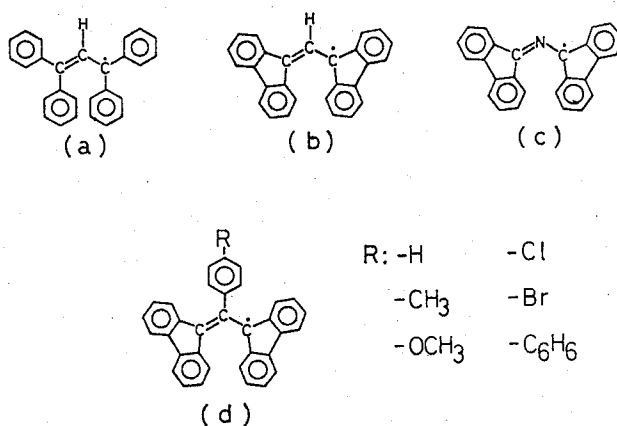


Fig. 1. Molecular structures of the tetraaryl allyl radicals: a) TPA b) BDA c) BDAA d) BDPA-type

ESR and ENDOR Spectra of BDPA and its Derivatives

Table I. Physical Constants and Elemental Analyses

	Mp ^{a)} (°C)	Obsd Calcd	C	H	N
BDA	244.4–245.5		94.85	5.01	
	245–246 ¹⁰⁾		95.00	5.00	
BDAA	270.0–271.5		90.91	4.91	3.80
	270–272 ¹¹⁾		91.62	4.71	3.78
BDPA	231–233 ⁴⁾		94.65	5.25	
			95.02	4.89	
<i>p</i> -Me-BDPA			94.54	5.61	
			94.63	5.37	
<i>p</i> -MeO-BDPA	238–240 ⁴⁾		91.93	5.35	
			91.25	5.18	
<i>p</i> -Cl-BDPA	269–271 ⁴⁾		87.59	4.43	
			87.69	4.46	
<i>p</i> -Br-BDPA	268–270 ⁴⁾		79.98	3.87	
			79.84	4.06	
<i>p</i> -Phe-BDPA	278–280 ⁴⁾		94.78	5.03	
			94.89	5.11	
TPA			92.98	5.58	
			93.86	6.14	

^{a)} Melting points are not corrected.

RESULTS AND DISCUSSIONS

I. ESR Spectra

The ESR spectra of each radical is shown in Fig. 2. The ESR spectra of BDPA and of its derivatives were very broad and no better-resolved spectrum has been observed under various conditions of the measurements. Approximate hyperfine splitting constants obtained are tabulated in Table II. The estimations of each proton position were worked out by the MO calculations and the spectrum simulations. On the other hand, an anomalously large proton hyperfine splitting (A_{β}^H) which has been observed in the ESR spectra of TPA and BDA is successfully explained by the following modified McConnell relation:¹³⁾

$$A_{\beta}^H = |Q_{CH}^H| \cdot \rho_{C\beta} + |B_{t-\pi}^H| \{ \cos^2(90-\theta) \cdot \rho_{Ca} + \cos^2(90-\phi) \cdot \rho_{C\gamma} \} \quad (1)$$

where Q_{CH}^H is $-22.5 \sim -29.0$ gauss and ρ_{Ca} , $\rho_{C\beta}$, and $\rho_{C\gamma}$ are 2π spin densities at the α -carbon (C_{α}), β -carbon (C_{β}), and γ -carbon (C_{γ}) respectively. Here, C_{α} and C_{γ} are the carbon atoms at the both sides of C_{β} in the allyl molecule and $B_{t-\pi}^H$ is a proportional constant for the twisted π -radical where the magnitude of B^H for the neutral radical is usually estimated to be $50 \sim 60$ gauss. The angles θ and ϕ are the mean values of the twisting angles of the $2p_z$ -orbitals on C_{α} and C_{γ} , respectively (see Fig. 3). The methine

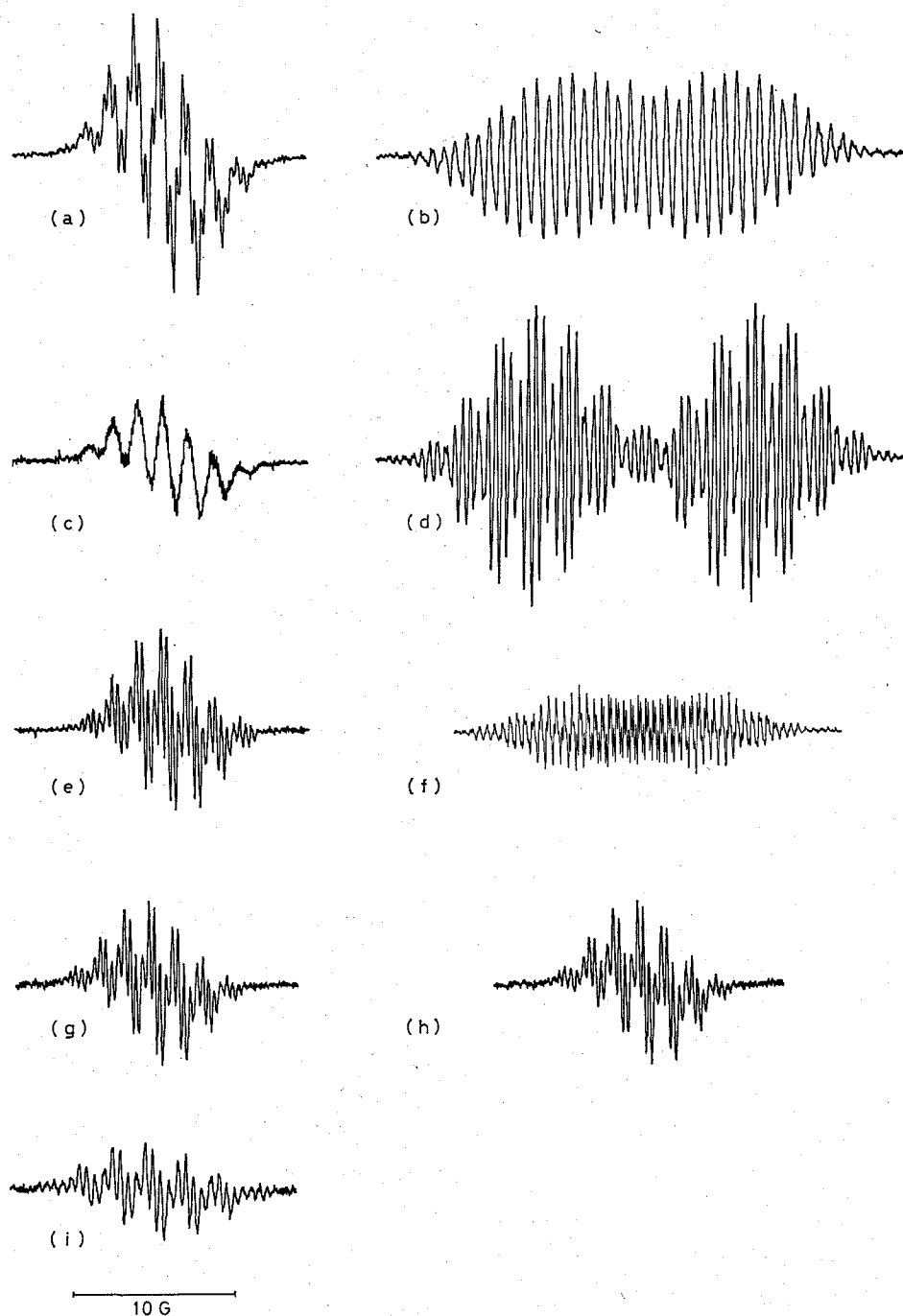


Fig. 2. ESR spectra of the tetraaryl allyl radicals: a) BDPA b) TPA
c) *p*-Me-BDPA d) BDA e) *p*-MeO-BDPA f) BDAA
g) *p*-Cl-BDPA h) *p*-Br-BDPA i) *p*-Phe-BDPA

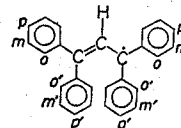
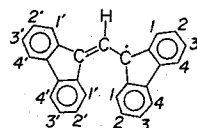
ESR and ENDOR Spectra of BDPA and its Derivatives

Table II. Hyperfine Splitting Constants (in gauss) and Twisted Angles of Allyl Skeleton

	A_β	$A_{1,1'}^H$	$A_{3,3'}^H$	$A_{2,2'}^H$	$A_{4,4'}^H$	Twisted angles of allyl skeleton ($\theta \approx \psi$)
BDA	13.4 ^{a)}	1.99	1.99	0.46	0.46	37°
(Ref. 4)	13.2 ^{a)}	1.92	1.86	0.48	0.36	
(Ref. 14)	13.2 ^{a)}	1.89	1.89	0.42	0.06	
BDAA	3.38 ^{b)}	1.89	1.89	0.44	0.30	
BDPA		1.96	1.96	0.67	0.67	
(Ref. 15)		2.2	2.2			
(Ref. 4)		1.8	1.8			
<i>p</i> -Me-BDPA		1.96	1.96			
<i>p</i> -MeO-BDPA		2.04	2.04	0.66	0.66	
<i>p</i> -Cl-BDPA		1.99	1.99	0.67	0.67	
<i>p</i> -Br-BDPA		1.99	1.99	0.66	0.66	
(Ref. 4)		1.86	1.75	0.44	0.33	
<i>p</i> -Phe-BDPA		1.98	1.98	0.67	0.67	
(Ref. 4)		1.86	1.65	0.44	0.33	
TPA	8.90 ^{a)}	1.95 ^{c)}	1.30 ^{d)}	0.64 ^{e)}		28°

Toluene solution at 25°C.

 a) A_β^H b) A_β^N c) $A_{o,p}^H$ d) $A_{o',p'}^H$

 e) $A_{m,m'}^H$


proton splitting (A_β^H) showed a marked positive temperature dependence as shown in Fig. 4. This temperature-dependent hyperfine splitting of the methine proton has also been explained presuming the model of the torsional vibration and the internal rotation of the allyl skeleton.¹⁶⁾ The allyl skeleton of BDPA-type radicals are also regarded as twisted allyls from the temperature dependence of the ENDOR spectra in these BDPA-type radicals as described in the following section, though no evidence of twisting of the allyl skeletons of BDPA-type radicals is found from the ESR spectra of these radicals.

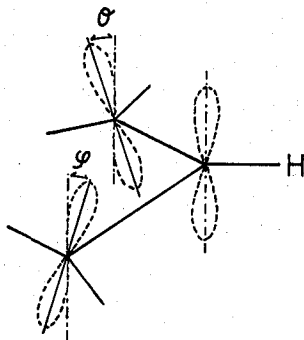


Fig. 3. Model of twisted allyl.

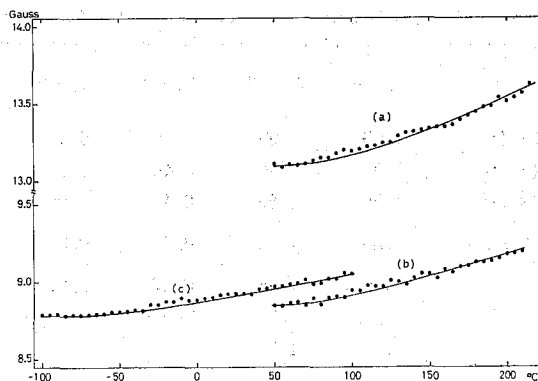


Fig. 4. Temperature-dependent hyperfine splittings of methine proton:
 a) BDA in liquid paraffin b) TPA in liquid paraffin
 c) TPA in toluene

II. ENDOR Spectra

The ENDOR spectrum of each radical in toluene solution is shown in Fig. 5. Since both BDA and BDAA are dimerized into diamagnetic substances at temperatures below -50°C , the ENDOR spectra of these radicals in toluene solutions could not be observed even at the suitable temperatures for observation.¹⁷⁾ The spectra of BDA, BDAA, and BDPA measured in liquid paraffin solutions are also shown in Fig. 5. Comparing the number of the absorption lines of BDPA-type radicals with those of BDA and BDAA, the smallest hyperfine splitting groups of BDPA-type radicals, which have not been observed in the ESR spectra, can clearly be identified to be due to the β -type protons. This fact indicates that the unpaired electron spreads over the β -aryl group, although the magnitude of the unpaired electron density is very small. Further, the spectra of BDPA and of *p*-Me-BDPA show the existence of two kinds of proton groups for the β -aryl protons. Taking into account the number of protons of methyl group in *p*-Me-BDPA, the larger and the smaller splittings in the small splitting groups are assigned to be due to the para- and ortho-protons of the β -aryl group, respectively. This assignment is supported by the fact that the smallest hyperfine splitting constants in BDPA and *p*-Me-BDPA are same in magnitude, compared with the other BDPA-type radicals which have no para-proton in the β -aryl group. Here it may be appropriate to assume that the splittings due to the meta-protons of the β -aryl group have not been observed¹⁸⁾ because the magnitude of the splittings is very small. The line shape at ca. 16.5 MHz varied with raising temperature and collapsed into an overlapped line in the temperature region above -65°C in toluene solution as is shown in Fig. 6. The proton hyperfine splitting constants thus obtained are shown in Table III, where the assignment of the hyperfine splitting constants are carried out in reference to the MO calculations. From this Table one can recognize that there exist four kinds of inequivalent protons in the biphenylene groups of each radical and moreover that the splitting constants due to the corresponding protons in these radicals are almost equal. Then it is concluded that the para-substitution of the β -aryl group does not affect spin density distribution.

On the other hand, Fessenden *et al.*²⁰⁾ confirmed three proton hyperfine splittings in the ESR spectrum of the allyl radical ($A_{\beta^{\text{H}}} = 4.06$ gauss, $A_{\alpha, \gamma^{\text{H}}} = 13.93$ gauss, and

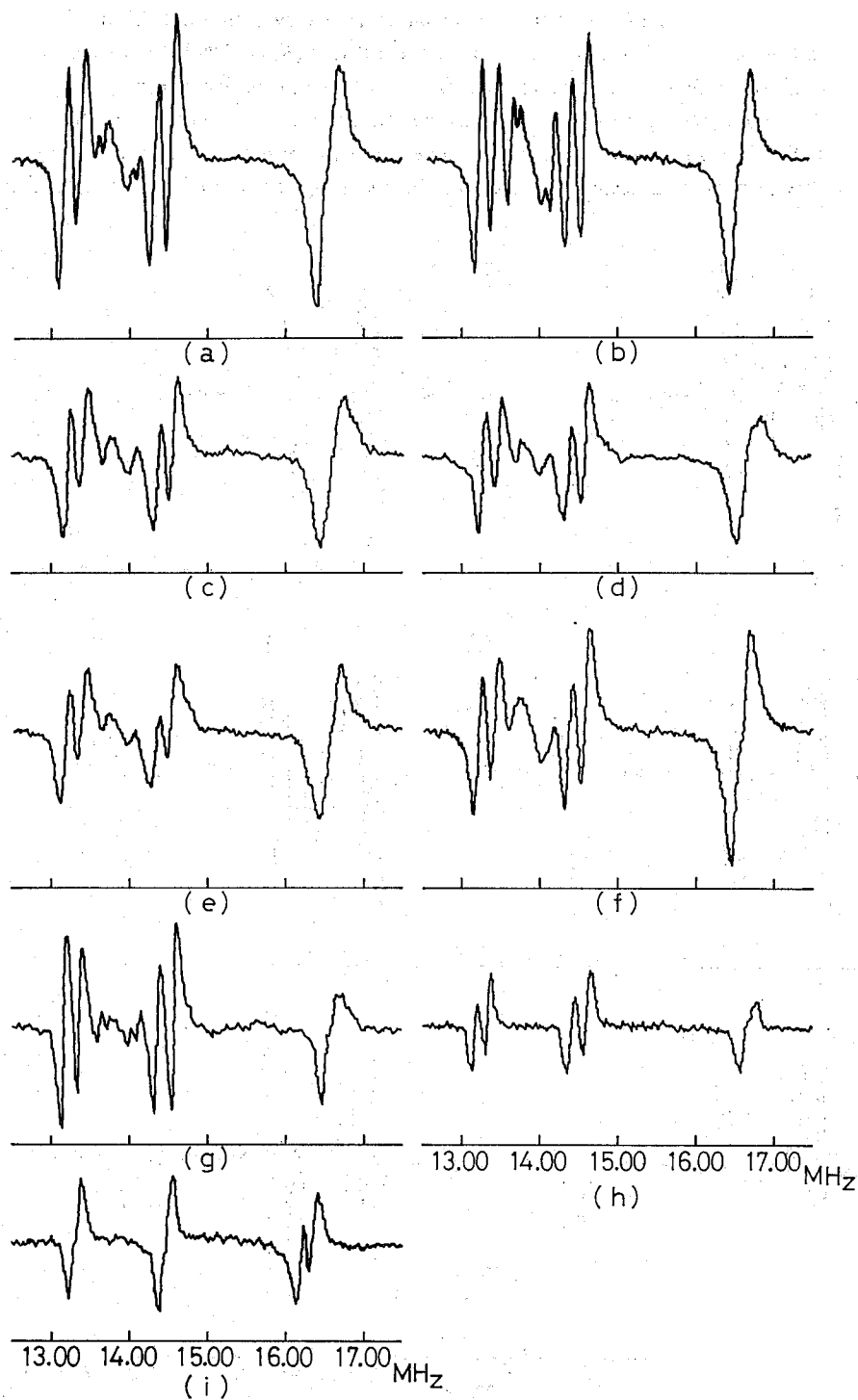


Fig. 5. ENDOR spectra of the bisdiphenylene allyl-type radicals:
 a) BDPA b) *p*-Me-BDPA c) *p*-MeO-BDPA d) *p*-Cl-BDPA
 e) *p*-Br-BDPA f) *p*-Phe-BDPA in toluene at -75°C g) BDPA
 h) BDA i) BDAA in liquid paraffin at 50°C .

$A_{\alpha, \beta}^H = 14.83$ gauss). This result indicates that there are two different kinds of the end protons in the allyl skeleton (Fig. 7). One of the authors (K. W.)¹⁶⁾ have also clarified the existence of two different kinds of phenyls in the TPA-type radicals from their ENDOR spectra. In connection with this fact, as has already been discussed in the previous paper,¹³⁾ these tetraaryl allyl radicals are never able to form the planar structure but to have the twisted allyl skeleton. In spite of the twisting of the allyl skeleton, a distance

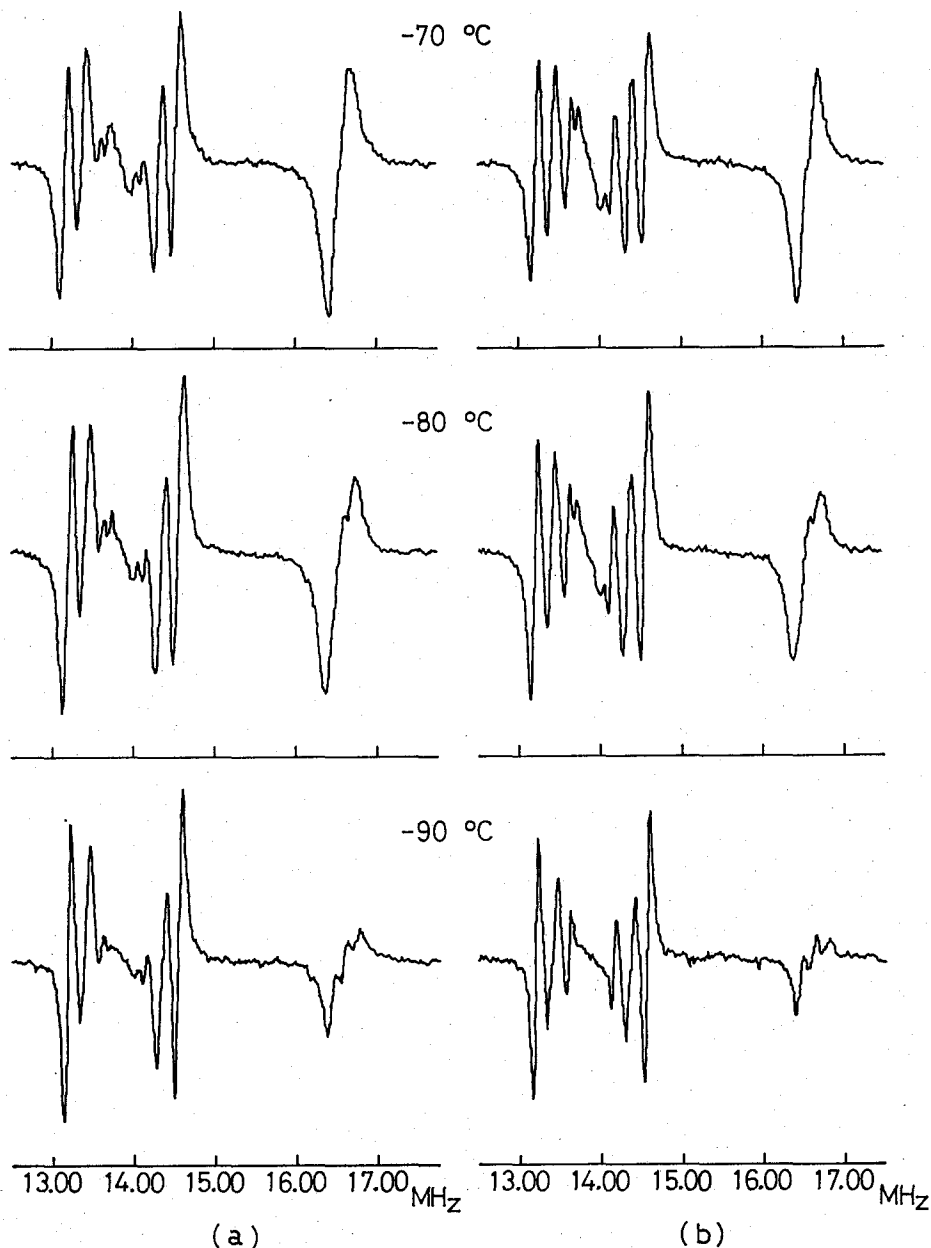


Fig. 6. Temperature dependence of ENDOR spectra of BDPA and *p*-Me-BDPA:
a) BDPA b) *p*-Me-BDPA in toluene

ESR and ENDOR Spectra of BDPA and its Derivatives

Table III. Observed and Calculated Splitting Constants (in gauss) and Energy of the Torsional Vibration of the Allyl Skeleton (in Kcal/mol)

	Temp. (°C)	$A_1^H A_1'^H$	$A_3^H A_3'^H$	$A_2^H A_2'^H$	$A_4^H A_4'^H$	A_{aryl}^H	ΔE
BDA	+40 ^{a)}	2.007	1.955	0.520	0.388		
	Calcd ^{b)}	1.890	1.593	0.324	0.054		
BDAA	+40 ^{a)}	1.782	1.564	0.437	0.396		
	Calcd ^{b)}	1.809	1.539	0.324	0.054		
BDPA	+40 ^{a)}	2.025	1.923	0.503	0.363	0.175	0.095
	-65	2.006	1.933	0.496	0.343	0.190	0.117
	-85	2.112	1.995	1.885	0.499	0.459	0.198
	(Ref. 9)	1.979	1.888	0.489	0.347	0.179	0.103
	Calcd ^{b)}	1.890	1.620	0.324	0.054	0.195	0.216
<i>p</i> -Me-BDPA	-65	2.000	1.917	0.500	0.343	0.190	0.124
	-85	2.099	1.975	1.859	0.501	0.349	0.200
<i>p</i> -MeO-BDPA	-65	2.076	1.938	0.484	0.346	0.138	2.7
	-85	2.115	1.994	1.888	0.494	0.351	0.132
<i>p</i> -Cl-BDPA	-65	2.075	1.959	0.491	0.330	0.117	2.2
	-85	2.113	1.982	1.909	0.499	0.346	0.120
<i>p</i> -Br-BDPA	-65	2.045	1.957	0.502	0.337	0.125	1.9
	-85	2.111	1.979	1.906	0.506	0.337	0.132
<i>p</i> -Phe-BDPA	-65	2.297	2.208	0.573	0.390	0.139	2.1
	-85	2.384	2.280	2.140	0.569	0.389	0.145

Toluene solution

a) liquid paraffin solution

b) Calculated splitting constants are obtained using the formula

$$A_{Cl}^H = |Q_{CH}^H| \cdot \rho_{Cl} \quad Q_{CH}^H = -27.0$$

where ρ_{Cl} are spin densities obtained by McLachlan's calculation¹⁹⁾ using the following parameters $\lambda=1.2$, $a_N=a+1.2\beta$, $\beta_{C-N}=0.9\beta$, $\theta=\psi=37^\circ$, and in BDPA-type radicals the tilted angle of the aryl attached to the C_β is assumed to be 30° .

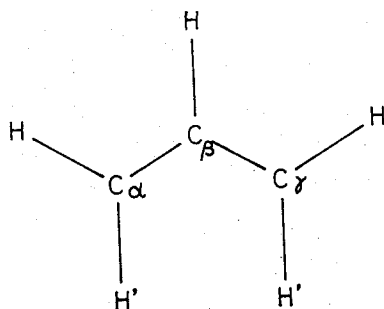
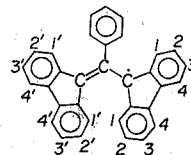


Fig. 7. Molecular structure of the allyl radical.

between the rings of B and C (interior rings) becomes much closer than that between the rings of A and D (exterior rings) or A and B. This model offers the rigorous theoretical basis to this ENDOR findings of the TPA-type radicals, that is, no equivalent spin distribution takes place between the exterior and interior rings (see Table IV). These conclusions of two kinds of the end protons in the allyl radical and two type aryl rings in the TPA-type radicals raise the problem: whether two phenylene rings in the biphenylene ring are really equivalent or not. However, two different kinds of equivalent aryl rings in the TPA-type radicals are held over the wide temperature region from -100 to $+100^\circ\text{C}$ in toluene solution by ESR spectra. Moreover, two different kinds of splitting constants of the end protons in the allyl radical are present over the wide temperature region from -130 to $+230^\circ\text{C}$ and only the methine proton splitting shows the positive temperature dependence.²¹⁾ On the contrary, in the BDPA-type radicals does occur the collapse of several hyperfine splitting lines at narrow temperature region in low temperatures and remains so over the wide higher temperature region. This result implies that the two phenylene rings in the biphenylene ring are equivalent. Further, in the bisdiphenylene allyl-type radicals, each diphenylene group attached to the α - or the γ -carbon is coplanar, and then each component phenylene group has no degree of free rotation each other, while it is not the case for TPA. Therefore, the temperature-dependent ENDOR spectra of the BDPA-type radicals as shown in Fig. 6 are regarded as being due to the time averaging effect of the twisting angles (θ, φ) which is caused by torsional vibration of the allyl skeleton. On the other hand, the MO calculations suggest that if a difference of the two twisting angles ($\theta \sim \varphi$) is tentatively assumed to be 10° , the difference between $A_{1,3^H}$ and $A_{1',3'^H}$ will become about 0.5 gauss but no noticeable difference will be seen between $A_{2,4^H}$ and $A_{2',4'^H}$. From this consideration one can conclude that the torsional vibration rate of the allyl skeleton ($\text{C}=\text{C}-\text{C} \rightleftharpoons \text{C}-\text{C}=\text{C}$) is so slow that the spectra which reflect the difference between θ and φ should be observed at quite low temperatures. At ordinary temperatures, however, the several lines near 16.5 MHz collapse into a single overlapped line, because of the fast torsional vibration of the allyl skeleton, while the two lines near 14.5 MHz remained unchanged as in Fig. 6. For such temperature dependence of ENDOR spectra, Hyde *et al.*²²⁾ proposed the rearranged Arrhenius equation as

Table IV. Observed and Calculated Splitting Constants of TPA (in gauss)

	A_{β^H}	A_{o^H}	A_{p^H}	A_{m^H}	$A_{o'^H}$	$A_{p'^H}$	$A_{m'^H}$
ESR	8.72	1.97	1.97	0.68	1.31	1.31	0.68
ENDOR	8.808	1.911	2.043	0.697	1.240	1.240	0.697
Calcd ^{a)}	9.142	2.079	1.944	0.729	1.458	1.377	0.513

Toluene solution at -80°C

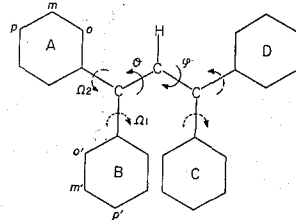
a) Calculated splitting constants are obtained using the formula

$$A_{o1^H} = |Q_{CH^H}| \cdot \rho_{C1} \quad Q_{CH^H} = -27.0$$

$$A_{\beta^H} = |Q_{CH^H}| \cdot \rho_{C1} + |B_{t-\pi}| \{ \cos^2(90-\theta) \cdot \rho_{Ca} + \cos^2(90-\varphi) \cdot \rho_{Ca} \}$$

$$|B_{t-\pi}| = 50, \quad \theta = \varphi = 28^\circ$$

where ρ_{C1} are spin densities obtained by McLachlan's calculation using the following parameters $\lambda = 1.2$, $\theta = \psi = 28^\circ$, $\Omega_1 = 35^\circ$, and $\Omega_2 = 15^\circ$.



$$\log_{10} 1/\tau\delta\omega = \log_{10} 2\nu_0/\delta\omega - \Delta E/2.3RT \quad (2)$$

$$1/\tau\delta\omega = 2^{-1/2} [1 - (\delta\omega_e/\delta\omega)^2]^{1/2} \quad (3)$$

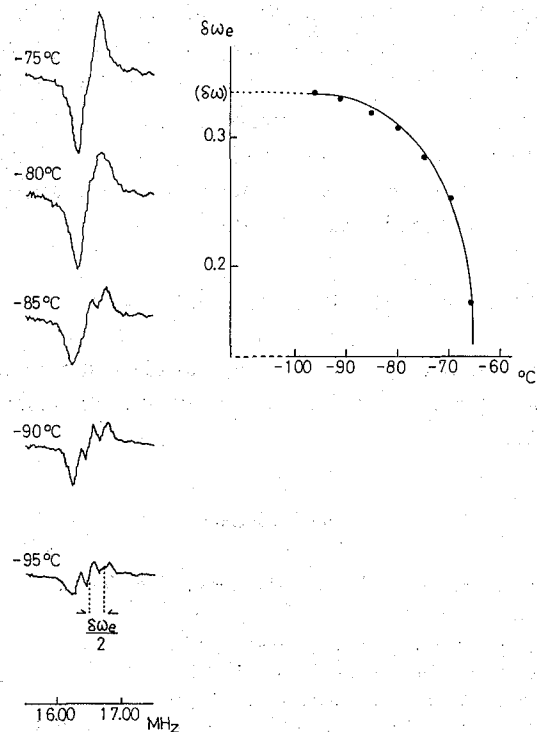


Fig. 8. Temperature dependence of the difference between two splittings ($\delta\omega_e$) near 16.5 MHz of BDPA in toluene.

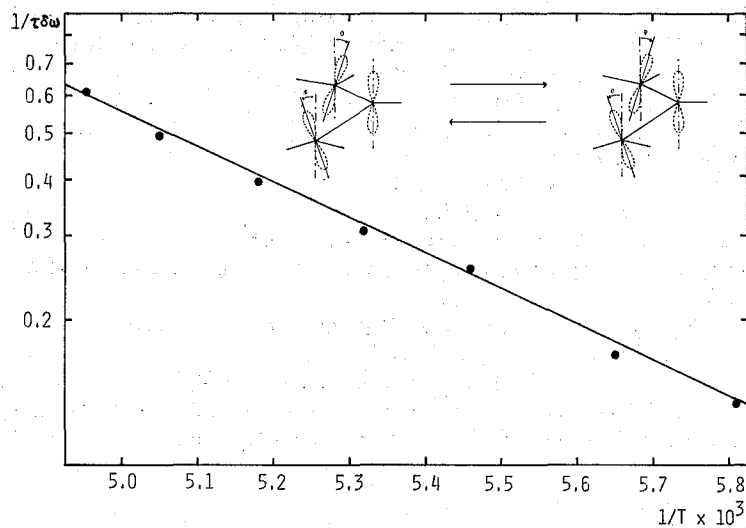


Fig. 9. Temperature dependence of torsional vibration rate of the allyl skeleton of BDPA in toluene.

where τ is the lifetime of a proton in a particular site, $\delta\omega$ the separation of the two lines in the limit of slow exchange, ν_0 the frequency factor, ΔE the activation energy of the torsional vibration of the allyl skeleton, R the gas constant, T the absolute temperature, and $\delta\omega_e$ the separation experimentally observed at the temperature. Using Eqs. (2), (3), and assuming the value of $\delta\omega$ as 0.34 MHz (Fig. 8), a straight line is obtained as in Fig. 9 for the BDPA case, from which the activation energy (ΔE) of the torsional vibration of the allyl skeleton ($\text{C}=\text{C}-\overset{\circ}{\text{C}} \rightleftharpoons \overset{\circ}{\text{C}}-\text{C}=\text{C}$) is estimated to be about 2.5 Kcal/mol. The activation energies of the other radicals are also listed in Table III. Judging from the fairly small magnitude of ΔE for the present radicals the torsional vibration of the allyl skeleton may be very sensitive to the temperature variation.

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